

## CHAPTER 2

### BONDS IN MATERIALS

#### Atomic bonding in solids

##### 2.1 Bonding forces and energies

On the basis of the knowledge of the inter atomic forces that bind the atoms together, many of the physical properties of materials can be predicted. The principles of atomic bonding can be well understood by considering the interaction between two isolated atoms as they are brought into close proximity from an infinite separation. At large distances the interactions are negligible. But as the atoms approach, each exert forces on the other. These forces are of two types, attractive and repulsive and the magnitude of these forces is a function of interatomic distance. The attractive force  $\vec{F}_A$  depends on the type of bonding that exists between the atoms. The magnitude of the attractive force varies with distance as shown in figure 2.1(a) when the outer electron shells of the two atoms begin to overlap, a strong repulsive force.  $\vec{F}_R$  comes into play. The net force  $\vec{F}_N$  between the atoms is thus becomes the sum of both attractive and repulsive forces; that is

$$\vec{F}_N = \vec{F}_A + \vec{F}_R \quad \dots \dots (1)$$

When  $\vec{F}_A$  and  $\vec{F}_R$  are equal and opposite the net force is zero; that is

$$\vec{F}_A + \vec{F}_R = 0 \quad \dots \dots (2)$$

In this context the atoms are said to be in equilibrium state. In this situation the atoms are separated by an equilibrium distance  $r_0$  shown in figure 2.1(b).

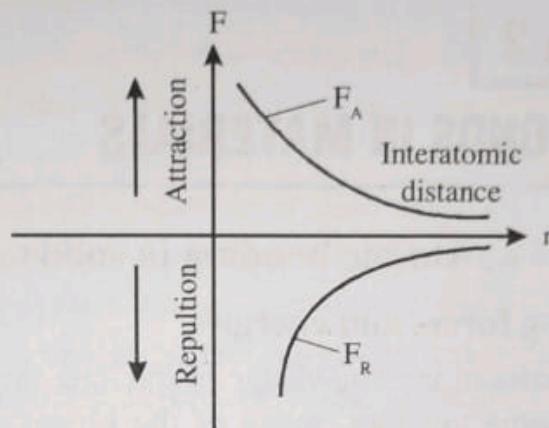


Figure 2.1(a)

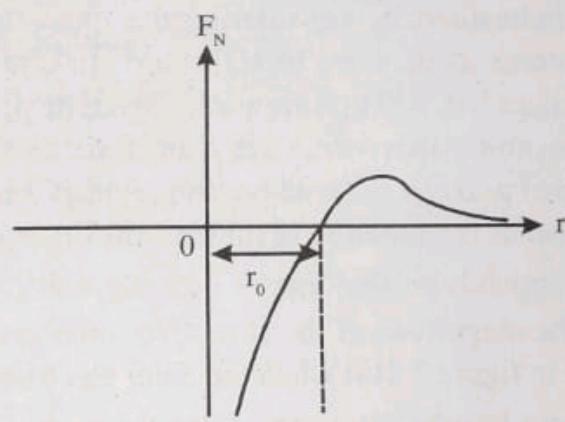


Figure 2.1(b)

For many atoms  $r_0$  is approximately 0.3nm. Sometimes it is more convenient to work with potential energies ( $U$ ) between two atoms rather than forces. Mathematically  $U(r)$  and  $F(r)$  are related by

$$U(r) = \int F(r) dr \quad \dots \dots (3)$$

For atomic systems

$$U_N(r) = \int_{\infty}^r F_N(r) dr \quad \dots \dots (4)$$

Substituting for  $F_N$  from equation 1.1, we get

$$U_N(r) = \int_{\infty}^r F_A dr + \int_{\infty}^r F_R dr$$

$$U_N(r) = U_A(r) + U_R(r) \quad \dots \dots (5)$$

Where  $U_N(r)$ ,  $U_A(r)$  and  $U_R(r)$  the net potential energy, attractive potential energy and repulsive potential energy respectively.

The variation of all  $U(r)$  with interatomic distance is shown in figure 2.1(c) and 2.1(d).

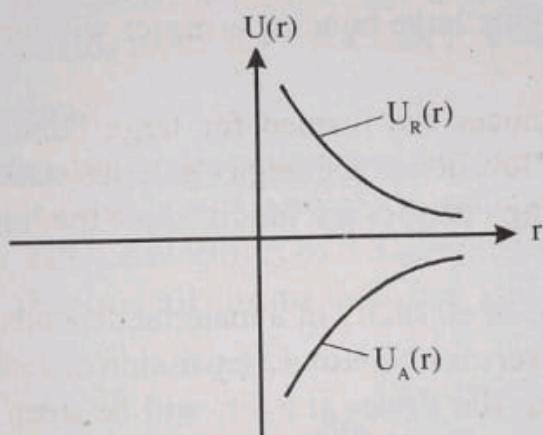


Figure 2.1(c)

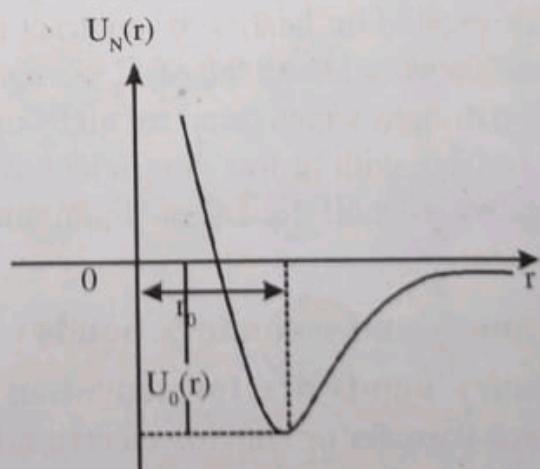


Figure 2.1(d)

atoms, we get almost the same shape for real materials formed by large number of atoms and so many interactions present. The bonding energy  $E_0$  varies from material to materials. Some of the materials (properties gathered from the shape of the curve and bonding energy is given below.

1. Material having large bonding energies will have high melting points.
2. Solid substances are formed for large bonding energies, whereas for low bonding energies gaseous states are formed. If the bonding energies are intermediate the liquid states are formed.
3. The modulus of elasticity of a material depends on the shape of the force versus interatomic separation distance graph. For stiff materials the slopes at  $r = r_0$  will be steep. For flexible materials the slopes at  $r = r_0$  are shallower.
4. The coefficient of linear expansions (how much the material will expand on heating or contract on cooling) of materials are related to the shape of  $U_0$  versus  $r_0$  curve. A narrow deep troughs which occur for high bonding energies, no correlates with a low coefficient of thermal expansion and relatively small dimensional alterations for changes in temperature.

## 2.2 Primary and secondary bonds

**Primary bonds are formed when the bonding process involves a transfer or sharing electrons between atoms to form a more stable electron configuration.**

There are three different types of primary bonds found in solids. They are (i) ionic bonding (ii) covalent bonding and (iii) metallic bonding.

**Secondary bonds are from the subtle attraction forces between positive and negative charges.** There is no transfer or sharing of electrons involved in secondary bonds. They are usually formed when an uneven charge distribution occurs, creating what is known as a dipole. The total charge is zero, but there is slightly more positive or negative on one end of the atom than on the other. There are three types of secondary bonding arising from different interactions. They are (i) dipole interactions (ii) hydrogen bonding interactions and (iii) molecule - molecule interactions.

### Ioning bonding

Ionic bonding is found in compounds composed of both metallic and non-metallic elements. Atoms of a metallic element can easily give up their valence electrons to the non-metallic atoms. In the process of sharing all atoms acquire stable or inert gas configurations, in addition each one becomes ions. Sodium chloride is an example of ionic material. A sodium atom gives out its one valence electron to chlorine atom. As a result sodium acquires a positive charge and chlorine acquires a negative charge. In sodium chloride, sodium and

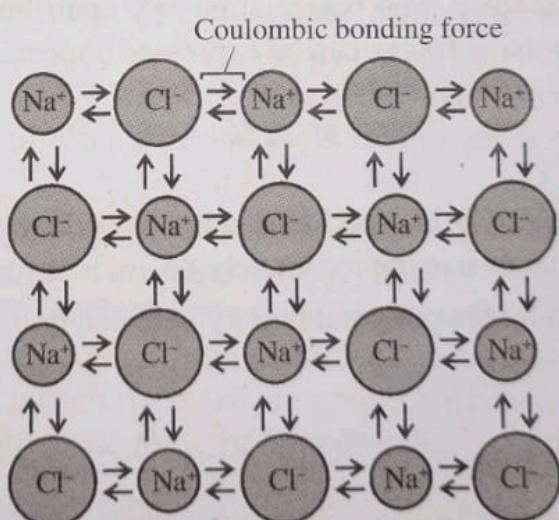


Figure 2.2: Schematic representation of ionic bonding in sodium chloride (NaCl)

chlorine exist as ions. This bonding (ionic) illustrate schematically in figure 2.2.

The attractive forces between different ions are Columbic in nature. For two isolated ions the attractive energy  $U_A$  is a function of the interatomic distance given by

$$U_A = \frac{(Ze)(-Ze)}{4\pi\epsilon_0 r} = -\frac{Z^2 e^2}{4\pi\epsilon_0 r}$$

or

$$U_A = -\frac{A}{r} \quad \dots\dots(6)$$

where  $A = \frac{Z^2 e^2}{4\pi\epsilon_0}$

Two ions cannot continuously approach each other under Coulomb attraction on account of exclusion principle. When they are at a certain small distance apart, they begin to repel each other with a force which increases rapidly with decreasing interatomic distance  $r$ . The potential energy contribution of the short range repulsive forces can be expressed approximately by

$$U_R = \frac{B}{r^n} \quad \dots\dots(7)$$

Here  $B$  is a constant and  $n$  is called repulsive exponent. The value of  $n$  is approximately 8.

The net potential energy between two adjacent atoms is given by

$$U_N = -\frac{A}{r} + \frac{B}{r^n} \quad \dots\dots(8)$$

From this we can evaluate the bonding energy  $U_0$  using the following procedure.

1. Differentiate  $U_N$  with respect to  $r$  and then set the resulting expression equal to zero. Which gives the equilibrium position  $r = r_0$ .
2. Put this value  $r = r_0$  in equation 1.8 to get  $U_0$ .

Bonding energies which generally range between 600 and 1500 kJ/mol or 3 and 8 eV/atom.

Other examples of ionic crystals are  $MgCl_2$ ,  $MgO$ ,  $CsCl_2$ ,  $KI$  and  $KO$ .

### Properties of ionic solids

1. All ionic solids have high melting points and boiling points. This is because more energy is needed to make the ions mobile, there being a necessity to overcome the strong electrostatic force of attraction created due to the ionic bond. This explains why ionic materials have high melting and boiling points.
2. Pure and dry ionic materials are insulators, because of the non-availability of free electrons. However in solution they conduct electricity because of the movement of charged ions. In a solution the ionic bond is weakened by the solvent molecules. Thus the ions become free to move about and thereby become conductors of electricity and the solutions are good electrolytes.
3. Ionic solids are easily soluble in polar solvent like water. This is because the molecules of the polar solvent interact strongly with the ions so as to reduce the attraction between the ions. Also the polar solvents possess high dielectric constants, for example, water has a high dielectric constant of 81. i.e., it will reduce the electrostatic force of attraction between the ions to  $\frac{1}{81}$  of the original value.

Ionic materials are insoluble in non-polar solvents benzene ( $C_6H_6$ ), carbon tetrachloride ( $CCl_4$ ), because their dielectric constants are very low.

4. High hardness and low conductivity are typical properties of these solids.
5. When subjected to stresses, ionic crystals tend to break along certain planes of atoms rather than to deform in a ductile fashion as metals do.
6. The magnitude of the ionic bonding is equal in all directions around an ion, hence it is termed non-directional.

### Covalent bonding

**The covalent bond is formed by sharing of pairs of valence electrons between like atoms rather than by electron transfer.**

A simple example of covalent bonding is found in the chlorine molecule. Here the outer shell of each chlorine atom possesses seven electrons. Each chlorine atom would like to receive one electron and thus form a stable octet. This can be done by sharing of two electrons between pairs of chlorine atoms, thereby producing stable diatomic molecules. In other words, each atom contributes one electron for the sharing process. See figure 2.3.

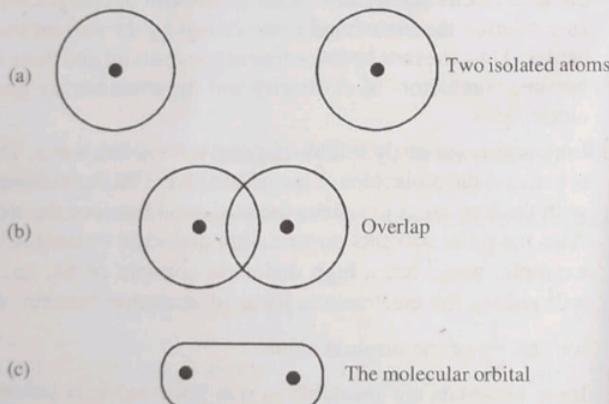


Figure 2.3: Molecular orbital from orbitals

Covalent bonding is schematically illustrated in figure 2.4. The carbon atom has four valence electrons, whereas each of four hydrogen atom has single valence electron. Each hydrogen atom can acquire a helium electron configuration (two is valence electrons) when the carbon atom shares with it one electron. The carbon atom now has four additional shared electrons one from each hydrogen, for a total of eight valence electrons, which is the electron structure of neon. The covalent bond is directional; that is it is between specific atoms and may exist only in the direction between one atom and another that participates in the electron sharing.

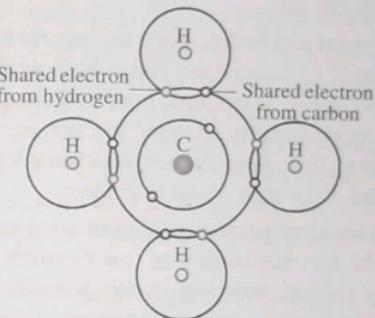


Figure 2.4: Schematic representation of covalent bonding in a molecule of methane ( $\text{CH}_4$ )

Many non metallic element molecules ( $\text{H}_2$ ,  $\text{Cl}_2$ ,  $\text{F}_2$  etc.) as well as molecules containing dissimilar atoms such as  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{HNO}_3$  and  $\text{HF}$  are covalently bonded. Further more, this type of bonding is found in solids such as diamond (carbon), silicon and germanium and other solid compounds such as gallium arsenide ( $\text{GaAs}$ ), indium antimonite ( $\text{InSb}$ ) and silicon carbide ( $\text{SiC}$ ).

The number of covalent bonds that is possible for a particular atom is determined by the number of valence electrons. For  $N^v$  valence electrons, an atom can covalently bond with at most  $8 - N^v$

other atoms. For example,  $N' = 7$  for chlorine and  $8 - 7 = 1$ , which means that one Cl atom can bond to only one other atom as in  $\text{Cl}_2$ . Similarly for carbon,  $N = 4$  and each carbon atom has  $8 - 4 = 4$  electrons to share.

### Properties of covalent

1. Covalent crystals tend to be hard and brittle and incapable of appreciable bending. These facts are understandable in terms of the underlying atomic forces. Since the bonds have well defined directions in space, attempts to alter them are strongly resisted by the crystal.
2. The melting point and boiling point are usually low as compared to those of ionic crystals. This is because the covalent bond is not so strong as the ionic bond and also because the atoms are less powerfully attracted towards each other the forces that attract them towards each other being Vander Waals forces, dipoles etc. which are quite weaker.
3. Most of the covalent substances do not conduct electricity because of the non-availability of free electrons or charged ions to carry current. However, certain substances like  $\text{HCl}$  which exhibit polarity in aqueous solutions behave like ionic substances and allow the passage of electricity.
4. Covalent substances are insoluble in polar solvents like water. However they are soluble in non polar solvents like benzene, carbon disulphide etc. This is because of the covalent nature of the solvent. However, the giant molecules are not soluble in any solvent because of the large size of the molecules.
5. A very interesting property of covalent crystals is the apparent lack of sensitivity of their physical properties to their bonding type. For example, carbon in the diamond structure is the hardest substance and has a very high melting point of

$>3350^\circ\text{C}$ . The hardness and melting point then decrease as we proceed to other elements from silicon to lead. Bismuth, for example, melts at about  $270^\circ\text{C}$ . The variation in the electrical properties is also pronounced. Diamond is a very good insulator. Silicon and germanium are semiconductors while tin is a good conductor and having low melting point and is very soft. Depending on the number of electrons shared, the bond length and bond energy vary. When the number of electrons shared is more, the bond length between the atoms is decreased and bond energy is increased.

6. Covalent compounds are mostly gases and liquids.

It is possible to have interatomic bonds that are partially ionic and partially covalent. In fact there are only very few compounds exhibit pure ionic or covalent bonding. For a compound, the degree of either bond type depends on the difference in their electronegativities. i.e., the greater the electron negativity, the more the ionic bond. Conversely, the closer the atoms are together it has smaller difference in electronegativity. The greater the degree of covalency.

The percentage ionic character of a bond between elements A and B (A being the most electronegative) may be approximated by the expression.

$$\text{Percentage ionic character} = [1 - e^{-0.25(X_A - X_B)^2}] \times 100 \text{ where } X_A \text{ and } X_B \text{ are the electronegativities for the elements A and B respectively.}$$

### Note

Electron negativity is the ability for an atom of a given chemical element to attract shared electrons in a covalent bond. An atom's electronegativity is affected by both its atomic number and the distance at which valence electrons reside from the charged nucleus. The higher the value of electronegativity, the more strongly that element attracts the shared electrons.

### Metallic bonding

Metallic bonding is found in metals and their alloys. In some respect, the metallic bond is similar to the covalent bond. A relatively simple model has been proposed that very nearly approximates the bonding scheme. Metallic materials that have one, two or at most three valence electrons. With this model, these valence electrons are not bound to any particular atom in the solid and are more or less free to drift throughout entire metal. They may be thought of as belonging to the metal as a whole or forming a "sea of electrons" or an electron cloud. The remaining non valence electrons and atomic nuclei form what are called ion cores, which possess a net positive charge equal in magnitude to the total valence electron charge per atom. A schematic illustration of metallic bonding is depicted in figure 2.5. The free electrons shield the positively charged ion cores from mutually repulsive electrostatic forces, which they would otherwise exert upon one another, consequently the metallic bond is unidirectional in character. In addition the free electrons act as a "glue" to hold their on cores together.

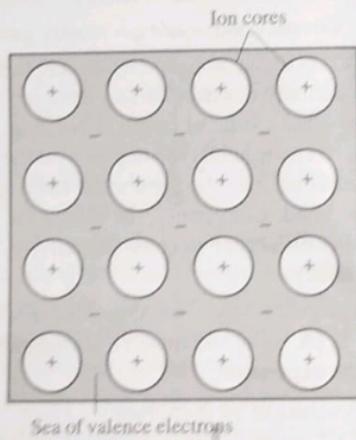


Figure 2.5: Schematic illustration of metallic bonding

### Properties of metallic bonding

- The bonding may be weak or strong. Bonding energies range from 68kJ/mol (0.7eV/atom) for mercury to 850kJ/mol (8.8eV/atom) for tungsten.
- Owing to the symmetrical arrangements of the positive ions in space lattice, metals are crystalline.
- The melting temperatures are -39°C to 3410°C for mercury and tungsten respectively.
- Since a large number of free electrons are available, metallic crystals have high electrical conductivity.
- Metallic crystals have higher thermal conductivity because of large number of free electrons.
- Metals are opaque to light since the light energy is absorbed by free electrons. Copper, sodium, silver and aluminium are some examples of metallic crystals.

### 2.3 Secondary bonding or Vander Waals bonding

Secondary bonds are weak in comparison to the primary bonds. The bonding energies are typically on the order of only 10kJ/mol (0.1eV/atom). Secondary bonding exists between virtually all atoms or molecules, but its presence may be obscured if any of the three primary bonding types is present. Secondary bonds do not generally involve the valence electrons. Secondary bonding is evidenced for the inert gases, which have stable electron structures and in addition between molecules in molecular structures that are covalently bonded.

Secondary bonding forces arise from atomic or molecular dipoles. In essence an electric dipole exists whenever there is some separation of positive or negative portions of an atom or molecule. The bonding results from the Columbic attraction between the positive end of one dipole and the negative region of an adjacent ones as indicated in figure 2.6.

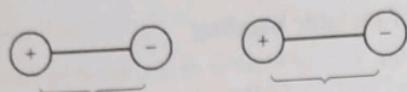


Figure 2.6: Schematic illustration of Vander Waals bonding between two dipoles

Dipole interactions occur in three ways:

- Interactions between induced dipoles.
- Interactions between induced dipoles and polar molecules.
- Interactions between some molecules that have hydrogen as one of the constituents. It is a special type of secondary bonding called hydrogen bonding. We discuss these one by one.

#### 2.4 Fluctuating induced dipole bonds

A dipole may be created or induced in an atom or molecule that is normally electrically symmetric; that is, the overall special distribution of the electrons in symmetric with respect to the positively charged nucleus as shown in figure 2.7(a). All atoms are experiencing constant vibrational motion that can cause instantaneous and short lived distortions of this electrical symmetry for some of the atoms or molecules and the creation of small electric dipoles as shown figure 2.7(b). One of the dipoles can in turn produce a displacement of the electron distribution of an adjacent molecule or atoms which induces the second one also to become a dipole that is then weakly attracted or bonded to the first; this is one type of Vander Waals bonding. These attractive forces may exist between large numbers of atoms or molecules, which force are temporary and fluctuate with time.

The liquitation and in some cases the solidification of the inert gases and other electrically neutral and symmetrical molecules such as  $H_2$  and  $Cl_2$  are realised because of this type of bonding. Melting and boiling temperatures are extreme low in materials for which

induced dipole bonding predominates; of all possible intermolecular bonds, these are the weakest.

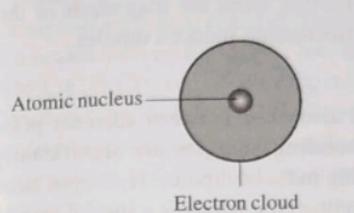


Figure 2.7(a): Electrically symmetric atom

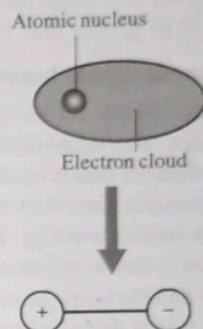


Figure 2.7(b): An induced atomic dipole

#### Polar molecule - Induced dipole bonds

Permanent dipole moments exist in some molecules by virtue of its unsymmetrical arrangement of positively and negatively regions. Such molecules are termed polar molecules. Figure 2.8 is a schematic representation of a hydrogen chloride. It possesses a permanent dipole due to the separation of net positive and negative charges of hydrogen and chlorine atoms forming HCl.

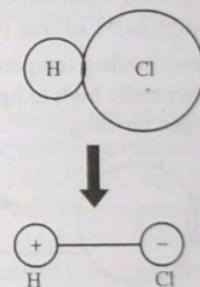


Figure 2.8 : Schematic representation of a polar hydrochloride (HCl)

Polar molecules can also induce dipoles in adjacent non polar molecules and a bond will form as a result of attractive force between the two molecules. Further more the magnitude of the bond will be greater than for fluctuating induced dipoles.

#### Permanent dipole bonds

Vander Waals forces will also exist between adjacent polar molecules. The associated bonding energies are significantly greater than for bonds involving induced dipoles. Hydrogen bonding is the strongest secondary bonding type which is a special case of polar molecular bonding. It occurs between molecules in which hydrogen is covalently bonded to fluorine (as in HF), oxygen (as in H<sub>2</sub>O) and nitrogen (as in NH<sub>3</sub>). For each one, the single hydrogen electron is shared with the other atom. Thus, the hydrogen end of the bond is essentially a positively charged bare proton that is unscreened by any electrons. This highly positively charged end of the molecule is capable of a strong attractive force with the negative end of an adjacent molecule as demonstrated in figure 2.9 for HF. In essence, this single proton forms a bridge between two negatively charged atoms. The magnitude of hydrogen bonding is generally greater than that of other types of secondary bonds and may be high as 51 kJ/mol (0.52 eV/molecule).

Melting and boiling temperatures for hydrogen fluoride and water are abnormally high in light of their low molecular weight due to hydrogen bonding.

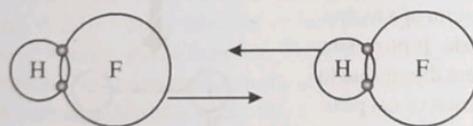


Figure 2.9: Schematic representation of hydrogen bonding in hydrogen fluoride (HF)

#### Molecules

Many of the common molecules are composed of group of atoms that are bound together by strong covalent bonds. Diatomic molecules such as F<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, etc. compounds such as H<sub>2</sub>O, CO<sub>2</sub>, HNO<sub>3</sub>, C<sub>6</sub>H<sub>6</sub>CH<sub>4</sub> etc. have strong covalent bonds. In the condensed liquid and solid states, bonds between molecules are weak secondary bonds. Consequently, molecular materials have relatively low melting and boiling temperatures. Most of those that have small molecules composed of a few atoms are gases at ordinary or ambient temperatures and pressures. On the other hand, many of the modern polymers, being molecular materials composed of extremely large molecules, exist as solids; some of their properties are strongly dependent on the presence of Vander Waals and hydrogen secondary bonds.

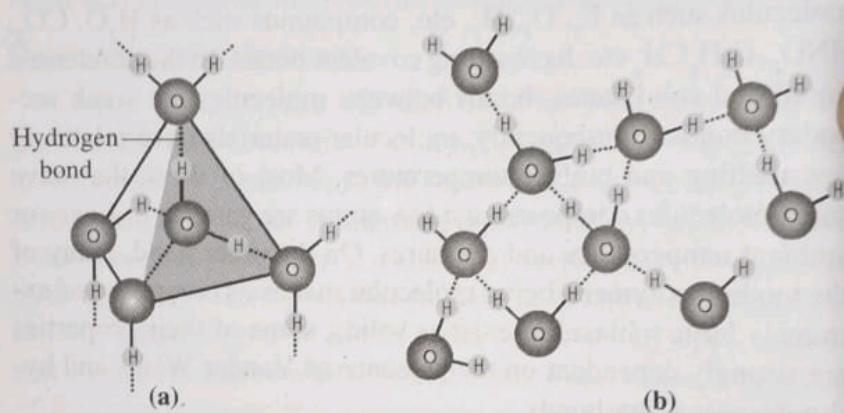
#### Anomalous volume expansion of water

Most of the liquids freeze to solids, the solid substances experience an increase in density, correspondingly there is a decrease in volume. One exception is water. Water upon freezing shows an anomalous behaviour of expansion. This expansion is approximately 9%. This behaviour may be explained on the basis of hydrogen bonding.

#### Explanation

Each H<sub>2</sub>O molecule has two hydrogen atoms that can bond to oxygen atoms; further more its oxygen atom can bond to two hydrogen atoms of other H<sub>2</sub>O molecules. Thus, for solid ice, each water molecule participates in four hydrogen bonds as shown in the three dimensional schematic of figure 2.10. Here hydrogen bonds are denoted by dashed lines and each water molecule has 4 nearest neighbour molecules. This structure is relatively open, i.e., the molecules are not closely packed together and as a result density is comparatively low. Upon melting this structure is partially destroyed, such that water molecules become more

closely packed together at room temperature the average number of nearest neighbour water has increased from 4 to 4.5. This leads to an increase in density or decrease in volume.



**Figure 2.10:** The arrangement of water ( $\text{H}_2\text{O}$ ) molecules in  
(a) solid ice and (b) liquid water

Anomalous expansion of water on freezing explains several natural occurring such as

- Why ice bergs float; because of density decrease.
- Why in cold countries it is necessary to add antifreeze to an automobile's cooling system. It is due to the expansion, cracking may occur.
- Why freeze thaw cycles break up the pavement streets and cause potholes to form.

#### Example 1

The net potential energy between two adjacent ions  $U_N$  is given by

$$U_N = -\frac{A}{r} + \frac{B}{r^n}$$

Calculate the bonding energy  $U_0$ .